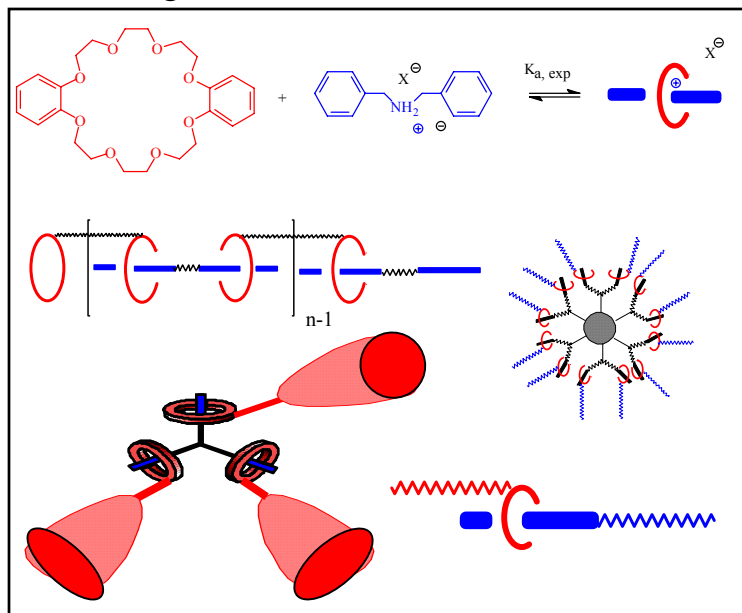


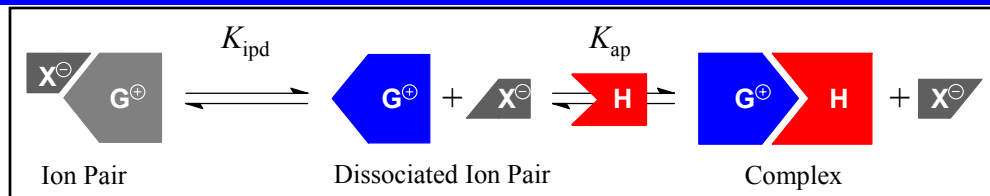
# Host-Guest Complexation for Self-Assembled Polymers

## Harry W. Gibson, DMR-0097126

We introduced self-assembled dendrimers,<sup>1,2a</sup> linear<sup>2</sup> and fullerene-cored star<sup>3</sup> polymers and block copolymers<sup>4</sup> based on pseudorotaxane formation (below) between various macrocyclic hosts and guest salts.



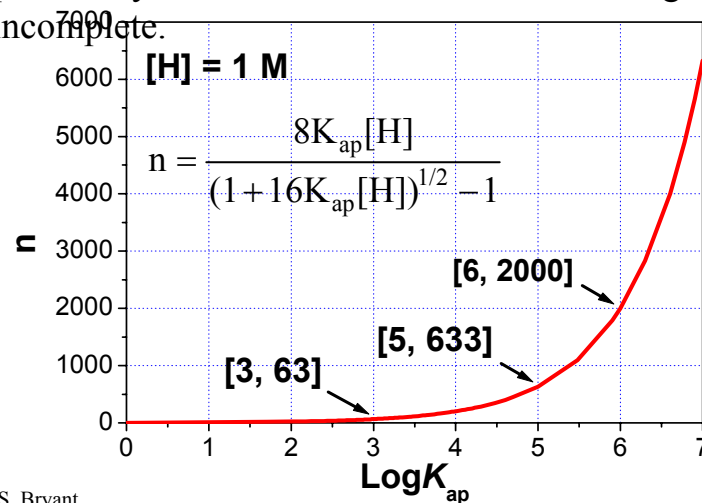
To better understand and predict the behavior of such supramolecular systems, fundamental host/guest equilibria have been explored.<sup>5</sup>



•We *proposed* a model which accounts for ion pairing as well as electrolyte activities in host/guest systems (above)

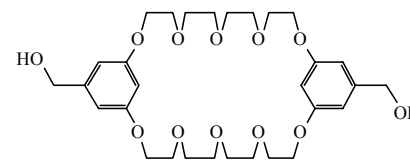
•We *showed* that association constants for complex formation ( $K_{ap}$ ), ion pair dissociation constants ( $K_{ipd}$ ), and activity coefficients may be readily *derived* from a series of well-designed experiments over a range of concentrations, and *determined* that previously used methods for determining “ $K_{a,exp}$ ” values are incomplete.

The degree of polymerization,  $n$ , in a self-assembled polymer is highly dependent upon  $K_{ap}$ , as the adjacent graph shows.

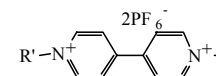


- (1) a) H. W. Gibson, N. Yamaguchi, L. Hamilton, J. W. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 4653-4665. b) J. W. Jones, W. S. Bryant, A. W. Bosman, R. A. J. Janssen, E. W. Meijer, H. W. Gibson, *J. Org. Chem.* **2003**, *68*, 2385-2389.
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To assist in folding of bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 (**1**) to complex paraquats (**2**) we used ditopic species that hydrogen bond to the OH groups; this results in  $\sim 10X$  increases in  $K_a$ .<sup>6</sup> To provide preorganized hosts, we *designed and synthesized* new bicyclic species, cryptands. The simplest one (**3**) resulted in a 100X increase in  $K_a$  relative to **1**.<sup>7</sup> Based on analyses of the X-ray structures we designed and prepared **4**, which contains a pyridyl N-atom in a position for H-bonding to the  $\beta$ -protons of the paraquat guest; **4** very strongly binds paraquat **2a** with  $K_a > 10^6 \text{ M}^{-1}$ ,  $\sim 10,000X$  that of **1**! Its X-ray structure shows the interaction between the pyridyl N and the  $\beta$ -protons of the guest. As can be seen from the graph on the previous page, application of this system should be capable of producing supramolecular (i. e., noncovalent) polymers with more than 2000 repeat units!

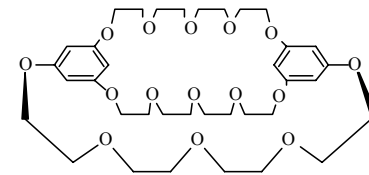


**1**

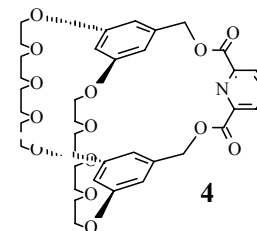


**a.**  $R=R'=CH_3$

**2**



**3**



**4**

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- (7) a) W. S. Bryant, J. W. Jones, P. E. Mason, I. Guzei, A. L. Rheingold, F. R. Fronczek, D. S. Nagvekar, H. W. Gibson, *Org. Lett.*, **1999**, *1*, 1001-1004. b) F. Huang, H. W. Gibson, W. S. Bryant, D. S. Nagvekar, F. R. Fronczek, *J. Am. Chem. Soc.* **2003**, *125*, 9367-9371. c) F. Huang, F. R. Fronczek, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 9272-9273.

## Broader Impacts of NSF Award, Harry W. Gibson, DMR-0097126

### Scholarship

- 5 undergraduates (3 females) have actively participated in research since 2000 under DMR funding
- 16 refereed papers and 6 preprints since 2000 based on DMR funding
- 1 US patent based on DMR funding
- 36 presentations, including 20 invited lectures (at universities, national and international meetings) since 2000 based on DMR funding
- 3 M. S. degrees awarded (Jason W. Jones, Feihe Huang, Amy Fletcher) since 2000 under DMR funding
- 5 postdocs (2 females) involved to various extents since 2000 under DMR funding

### Awards

- William Preston Award for best Master's Thesis at Virginia Tech, 2003, Feihe Huang, current Ph.D. candidate
- DOE Travel Award to Attend the 53<sup>rd</sup> Annual Meeting of Nobel Laureates, 2003, Jason W. Jones, current Ph.D. candidate
- 2 Departmental Graduate Research Excellence Awards: Jason W. Jones, Feihe Huang
- Cook Faculty Research Award, VT Chemistry Department, 2001, Harry W. Gibson,

**Industrial Connection:** LUNA Innovations, Inc.